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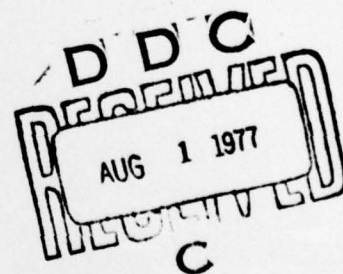
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Research Findings Resulting from this Grant

The research program carried out over the previous three year period in our laboratories was divided into four interrelated areas. The progress made in each area is summarized below.

1. Electrode Kinetics in the Presence of Little or no Supporting Electrode.

In experiments designed to determine the origin of the puzzling effects of ionic strength on the specific adsorption of most anions on positively charged mercury electrodes¹⁻⁴ we confirmed⁵ the previous reports that as the ionic strength of solutions of a single salt is lowered the anion adsorption adjusts itself so that the negative ionic charge due to the adsorbed anions just matches the positive electronic charge on the electrodes. Our experimental results led us to suggest that in sufficiently dilute solutions of many simple salts such as NaCl, NaBr, NaClO₄, NaNO₃, and NaN₃, the diffuse portion of the electrical double layer might be eliminated by means of this self-imposed delicate balance between ionic and electronic charges on the electrode surface.⁵ This possibility for eliminating diffuse double layers was pursued because it offered the hope of considerable simplification in electrode kinetic measurements where uncertainties in making "diffuse double layer corrections" are often the source of very large uncertainties in the kinetic parameters evaluated. Subsequent experiments^{6, 7} have confirmed the very close matches between positive electronic and adsorbed anionic charges with pure salt solutions at ionic strengths below about 10⁻² M. However, even small mismatches between the two kinds of surface charges (e.g., 0.1 - 0.2 $\mu\text{C cm}^{-2}$) result in relatively large potential drops across the diffuse layer (e.g., 10 - 50 mV) at the low ionic strengths required to produce the trend toward matching of the charges. Near misses turn out to be more likely than exact matches so that true elimination of the diffuse layer is rarely achieved. However, in the course of the experiments which had lead to this conclusion a number of heretofore unrecognized aspects of the behavior of the diffuse double layer at low ionic strengths have come to light and these are described and analyzed in reference 6.

2. Electrochemical Characterization of Reactants Attached to Electrode Surfaces.

In previous studies we have made extensive use of the double potential-step chronocoulometric technique⁸ to assay the concentrations of reactants adsorbed on electrode surfaces. Although this technique provides a rapid and reliable surface analysis, it is not designed to probe the detailed electrochemical behavior of the adsorbed reactants because the electrode potential is necessarily restricted to values far from the point at which reactants first begin to show electrochemical activity.

In recent work we have adapted the well known analytical technique of differential pulse voltammetry (polarography)⁹⁻¹¹ for use in examining the electrochemistry of adsorbed reactants. This technique delivers the electrochemical response at potentials near the polarographic half-wave potential or the cyclic voltammetric peak potential so that behavioral differences among reactants can be readily inspected. Of particular value has been the ability of the differential pulse technique to monitor the electrochemical responses of a single monolayer of reactant attached irreversibly to electrode surfaces.¹⁰ This capability offers numerous opportunities for further exploitation in studies of the surface chemistry of electrodes constructed from a variety of materials.

3. Improved Instrumentation for Experimental Electrode Kinetics

We have devoted a considerable effort to the construction and testing of a charge-injection (coulostatic)¹² apparatus which incorporates a Biomation transient recorder which is linked, in turn, to a minicomputer. The objective has not been the conventional attempt to see how large an electrode reaction rate could be measured. Instead, the instrument has been utilized in studies of reaction kinetics in solutions containing very little supporting electrolyte where problems with large uncompensated resistances require that kinetic data be obtained from open circuit measurements. The apparatus is also well suited for kinetic measurements with reactants that are confined to the electrode surfaces because of the large transient currents that result in such cases, even with reactants which yield much smaller rates when they are examined in homogeneous solution. For example, a one-electron reactant with a rate constant as small as 10^{-5} cm sec⁻¹ which produces a current of ca. 10^{-6} amp cm⁻² from a millimolar solution would yield a transient current of ca. 2×10^{-2} amp cm⁻² if it exhibited the same relative reactivity when present in the form of a monolayer ($\sim 10^{-9}$ moles cm⁻²) attached to the electrode surface. Such large currents present experimental difficulties because of the inevitable presence of some uncompensated resistance even in the presence of supporting electrolyte. Open circuit (coulostatic) measurements avoid this source of difficulty and this is the chief reason that the coulostatic apparatus has been constructed for use in kinetic measurements with adsorbed reactants.

4. Electrode Kinetics with Adsorbed Reactants

Our continuing efforts to deal with both the theory^{13,14} and experimental measurement^{15,16} of electrode kinetics with reactants attached to electrode surfaces result from the conviction that failure to take account of the chemistry of electrode surfaces is likely to lead to inadequate understanding of electrode processes as well as unrealized potential for electrocatalysis of sluggish reactions. Considerable progress has been achieved, particularly with respect to a more detailed formulation of acceptable rate law's for reactions involving adsorbed reactants¹³ and new experimental tactics for distinguishing between kinetic contributions from adsorbed and unadsorbed reactants.^{15,16} Experimental measurement of the adsorption and desorption rates of one class of

strongly adsorbing reactants has also proved possible¹⁷ and some chemical factors which may be responsible for the slow establishment of adsorption equilibrium have been suggested.

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J. Electroanal. Chem., 54, 55 (1974)

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Eu^{2+} and V^{2+} as Electrode Kinetic Probes of the Structure of the Diffuse Layer in Dilute Electrolytes

Fred C. Anson and Bruce A. Parkinson
J. Electroanal. Chem., in press

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